The Inverse Quantum Chemical Approach to Molecular Vibrational Properties

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General aim:

Structure $\Longleftrightarrow$ Property/Function

Here:

## Multitude of Properties $\longrightarrow$ Important Properties

Introductory Remarks: Theor. Vibrational Spectroscopy

- important tool for structural characterisation of molecules, if X-ray structures are not known, e.g., for
  - unstable systems
  - molecules in (aqueous) solution
  - heterogeneous, non-crystalline aggregates
- Interpretation of spectra difficult without theoretical support!
- $\Rightarrow$ solve time-independent nuclear Schrödinger equation (in Born–Oppenheimer approximation)

$$\left[-\frac{\hbar^2}{2} \nabla^\dagger \mathbf{M}^{-1} \nabla + E_{\text{el}}(\mathbf{R}) \right] |v^{\text{tot}}\rangle = E_{\text{tot}} |v^{\text{tot}}\rangle$$

- approximation of $E_{\text{el}}(\mathbf{R})$ is complicated and time-consuming!
- $\Rightarrow$ Focus on most important vibrations possible?
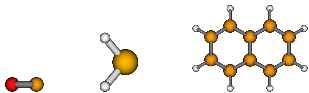 - $\Rightarrow$ circumvent deadwood by smart algorithms

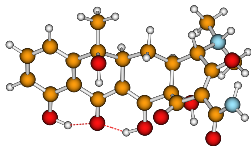# Methods for Different Molecule Sizes
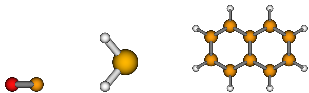
very small
detailed spectroscopic data
(rovibrational   coupling,
overtones, comb. bands)

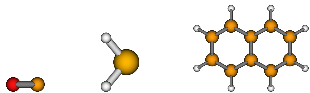# Methods for Different Molecule Sizes

very small

detailed spectroscopic data (rovibrational coupling, overtones, comb. bands)
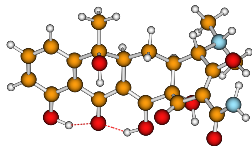

medium

complete vibrational spectra; occasionally: anharmonic corrections
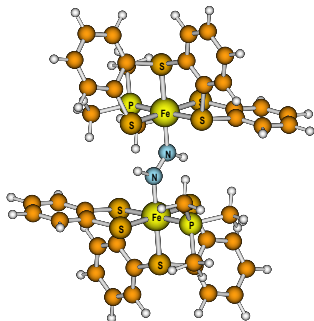
Methods for Different Molecule Sizes

very small
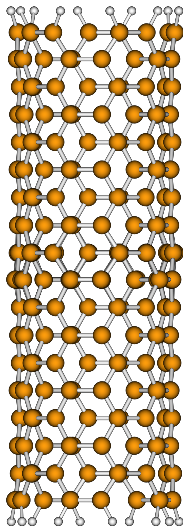detailed spectroscopic data (rovibrational coupling, overtones, comb. bands)

medium
complete vibrational spectra; occasionally: anharmonic corrections

large
data reduction necessary, intensities and/or frequencies only for selected vibrations

Vibrational Spectroscopy for Large Molecules:

The Standard Approach

Textbook: The harmonic approximation

- approximate electronic energy by truncated Taylor series

$$E_{el}(\{R_I\}) \approx E_{el}(\{R_I\}_0) + \sum_I^{3N} \left(\frac{\partial E_{el}}{\partial R_I}\right)_0 R_I + \frac{1}{2}\sum_{I,J}^{3N,3N} \left(\frac{\partial^2 E_{el}}{\partial R_I \partial R_J}\right)_0 R_I R_J$$

- Hamiltonian in harmonic approximation

$$-\frac{1}{2}\sum_I^{3N} \frac{\nabla_{R_I}^2}{M_I} + E_{el}(\{R_I\}_0) + \sum_I^{3N} \left(\frac{\partial E_{el}}{\partial R_I}\right)_0 R_I + \frac{1}{2}\sum_{I,J}^{3N,3N} \left(\frac{\partial^2 E_{el}}{\partial R_I \partial R_J}\right)_0 R_I R_J$$

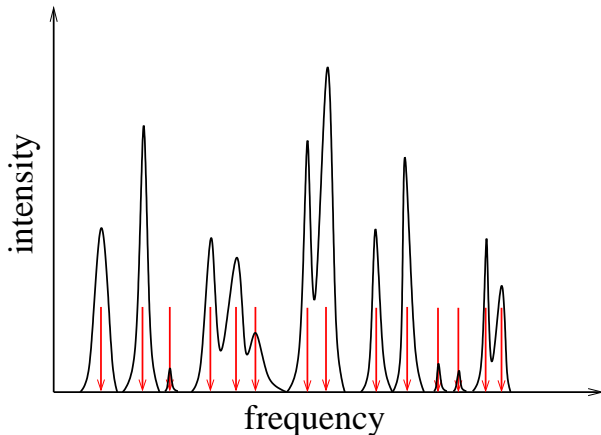- Equilibrium geometry $\Rightarrow \left(\frac{\partial E_{el}}{\partial R_I}\right)_0 = 0 \; \forall I$, mass-weighting (m)

$$\left[-\frac{1}{2}\sum_I^{3N} \nabla_{R_I^{(m)}}^2 + \frac{1}{2}\sum_{I,J}^{3N,3N} \left(\frac{\partial^2 E_{el}}{\partial R_I^{(m)} \partial R_J^{(m)}}\right)_0 R_I^{(m)} R_J^{(m)}\right]\chi = E_{vib}\chi$$

$\Rightarrow$ $3N$ coupled differential equations

$\rightarrow$ decouple by diagonalizing Hessian matrix $\{\partial^2 E_{el}/\partial R_I^{(m)} \partial R_J^{(m)}\}$
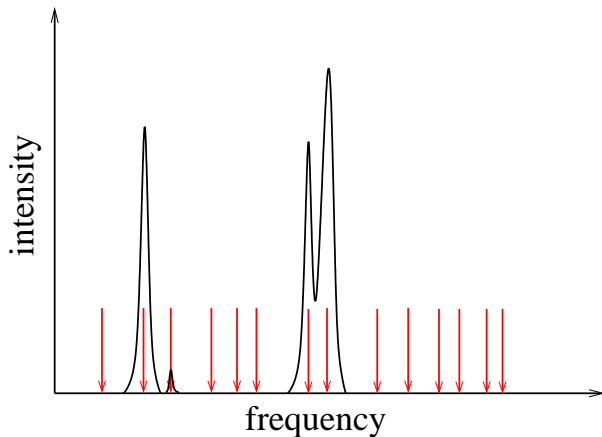
Spectra Calculation within the Harmonic Approximation

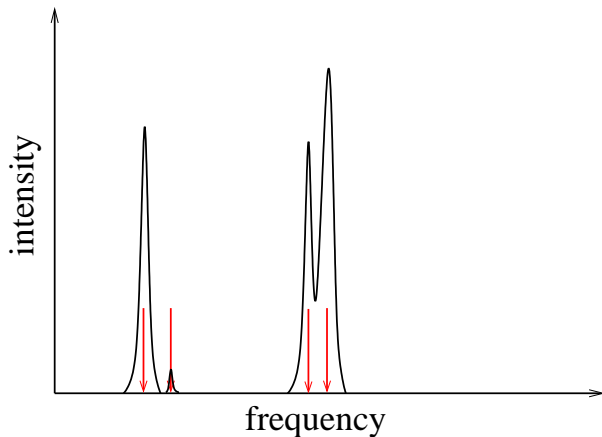J. Neugebauer, M. Reiher, C. Kind, B.A. Hess, *JCC 23* **2002** 895

download SNF program: http://www.reiher.ethz.ch/software/snf

Data Reduction for Large Molecules (1)

M. Reiher, J. Neugebauer, B. A. Hess, *Z. Phys. Chem. 217* **2003** 91

Data Reduction for Large Molecules (2)

M. Reiher, J. Neugebauer, *J. Chem. Phys. 118* **2003** 1634

An example for which this would be useful

Schrock's Dinitrogen Fixation Complex

(recall David Beratan's remark on Haber-Bosch vs. nitrogenase catalysis and Ping Liu's talk on heterogeneous catalysis)

The Schrock catalyst

- Reductant: metallocenes $Cr(cp^*)_2$, $Co(cp^*)_2$ and $Co(cp)_2$ as electron source
- Acid: 2,6-Dimethyl pyridinium as proton source
- Bulky ligand prevents dimerization
- Isopropyl and terphenyl groups crucial
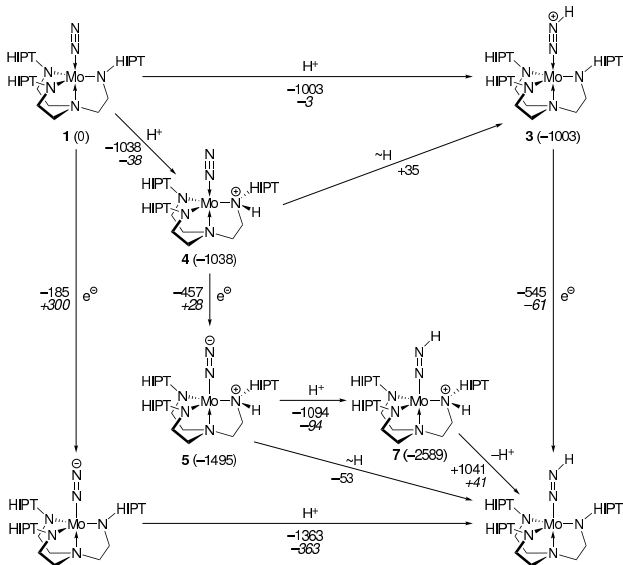- W, V or Cr do not work[a]

(HIPT)
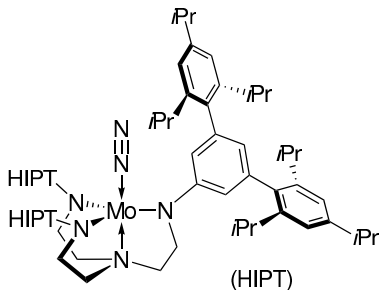
Theory:
Inorg. Chem. *44* **2005** 9640;
Chem. Eur. J. *11* **2005** 7448;
Inorg. Chem. *47* **2008** 3643;
Inorg. Chem. *48* **2009** 1638

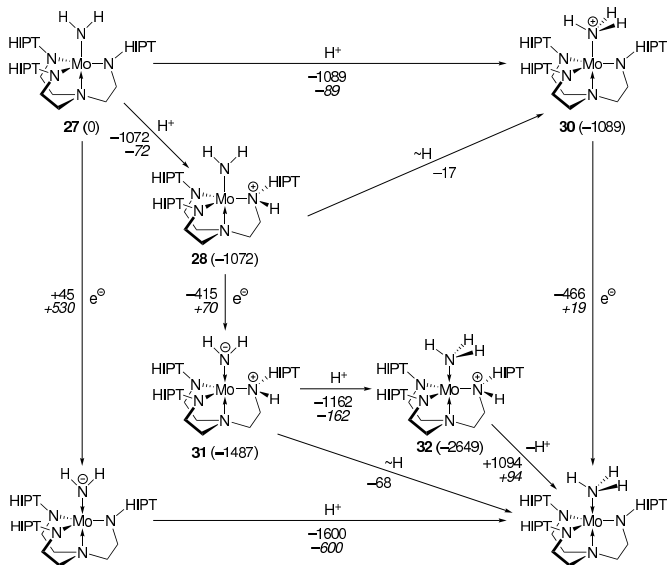[a]Experiment: D.V. Yandulov, R.R. Schrock, Science *301* **2003** 76; ... and many more; Early review: R.R. Schrock Acc. Chem. Res. *38* **2005** 955
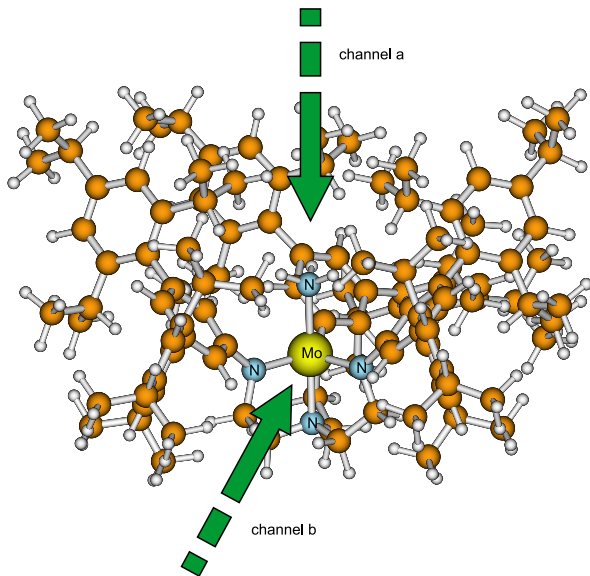
First step: Transfer of the **first** electron / proton pair

Last step: Transfer of the **sixth** electron / proton pair

Entry channels for N$_2$

channel a

Mo

N

N

N

N

channel b

One of the six-coordinate intermediates[1]
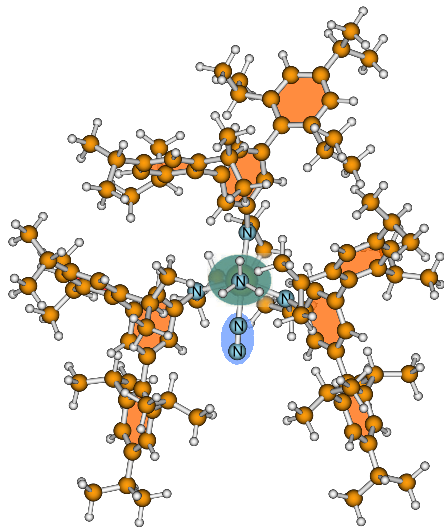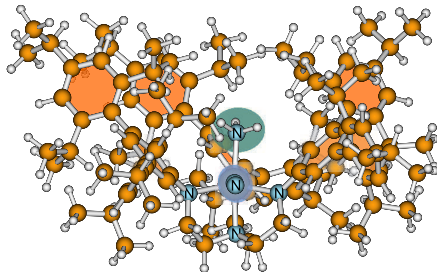
top view   side view

[1]S. Schenk, B. Kirchner, M. Reiher, Chem. Eur. J. *15* **2009** 5073

IR Spectra: N_2-complex vs. two 6-coordinate intermediates
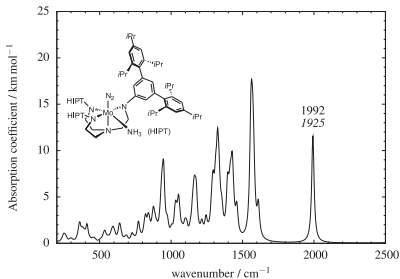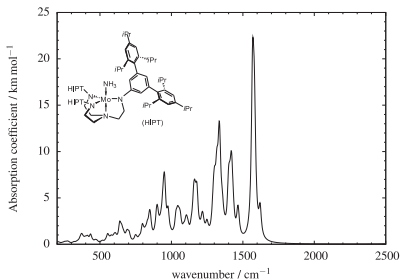
Exchange reaction energy vs. N≡N stretching vibration

Screening of different ligands for catalyst improvement:
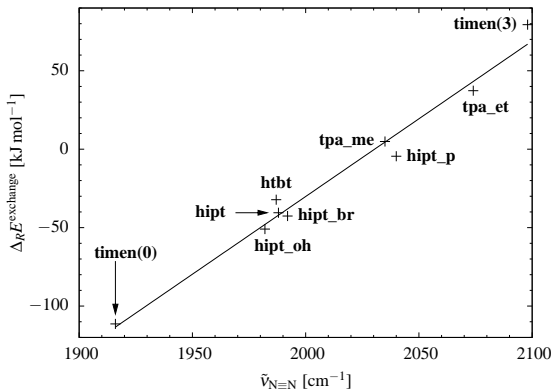
⟹ Such a screening requires only a single vibration out of about 600 !

Standard Approach versus New Inverse Methods

- The standard approach to diagonalize the Hessian is quite expensive

  because all entries in this matrix are expensive to calculate

  — besides: this is brute force without brains
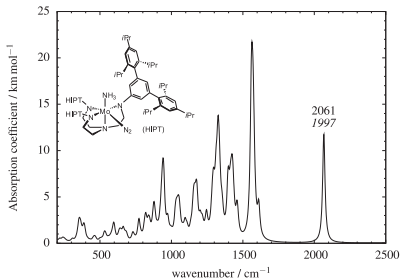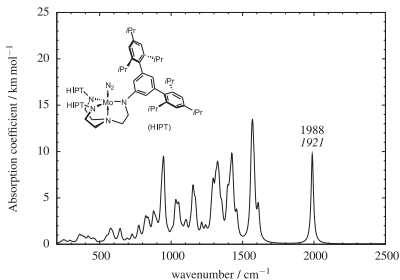
- Devise *smart* algorithms that are also faster:

  - Provide a guessed vibration and refine it:
    MODE-TRACKING

  - Converge only those collective vibrations that pick up intensity:
    INTENSITY-TRACKING

  Review of both:

  K. Kiewisch, S. Luber, J. Neugebauer, M. Reiher, Chimia *63* **2009** 270

Mode-Tracking: Concept

- Aim: Calculate relevant normal modes only

$\rightarrow$ Mode-Tracking — Selective calculation of vibrational frequencies and normal modes from eigenpairs of the Hessian matrix through subspace iteration.

- Subspace iteration is not only useful for diagonalization of huge matrices, but also for small matrices with expensive entries!

- Instead of direct solution of
$$[\mathbf{H} - \lambda_\mu]\mathbf{q}_\mu = \mathbf{0}$$
solve
$$[\mathbf{H} - \lambda_\mu^{(i)}]\mathbf{q}_\mu^{(i)} = \mathbf{r}_\mu^{(i)}$$
iteratively for a few eigenpairs until $\mathbf{r}_\mu^{(i)} \to 0$

M. Reiher, J. Neugebauer, J. Chem. Phys. *118* **2003** 1634

Sketch of the Mode-Tracking Algorithm

SUBSPACE ITERATION

coarse–grained parallelization

fine–grained parallelization possible

converged ?

C_1

+ C_2

+ ...
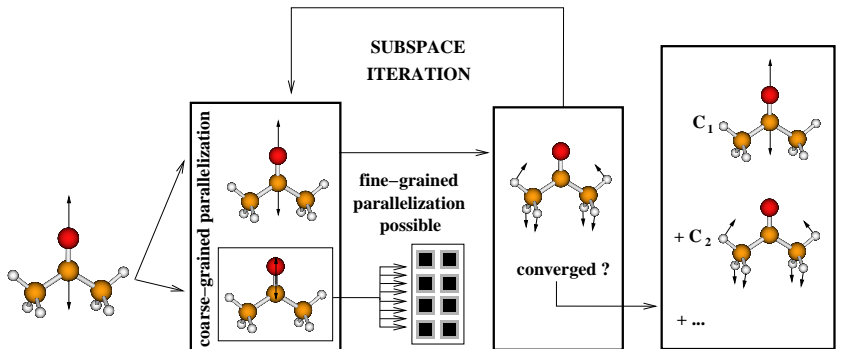
provide initial guess for normal coordinates as first basis vectors

(several modes possible)
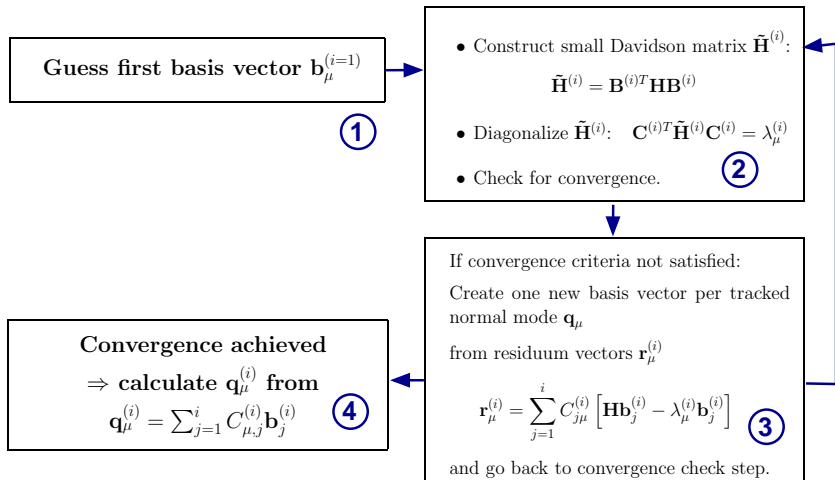
distribute single points to slave nodes

calculate gradient save intermediate data **for restart facility (coarse/fine–grained)**

calculate approximate frequencies, residua, preconditioner, new basis vector

obtain normal coordinate as linear combination of basis vectors

use mode–wise approach for intensities

Mode-Tracking Algorithm

Guess first basis vector $\mathbf{b}_\mu^{(i=1)}$ ①

- Construct small Davidson matrix $\tilde{\mathbf{H}}^{(i)}$:
$$\tilde{\mathbf{H}}^{(i)} = \mathbf{B}^{(i)T}\mathbf{H}\mathbf{B}^{(i)}$$
- Diagonalize $\tilde{\mathbf{H}}^{(i)}$: $\quad \mathbf{C}^{(i)T}\tilde{\mathbf{H}}^{(i)}\mathbf{C}^{(i)} = \lambda_\mu^{(i)}$
- Check for convergence. ②

If convergence criteria not satisfied:

Create one new basis vector per tracked normal mode $\mathbf{q}_\mu$

from residuum vectors $\mathbf{r}_\mu^{(i)}$

$$\mathbf{r}_\mu^{(i)} = \sum_{j=1}^{i} C_{j\mu}^{(i)}\left[\mathbf{H}\mathbf{b}_j^{(i)} - \lambda_\mu^{(i)}\mathbf{b}_j^{(i)}\right] \quad ③$$

and go back to convergence check step.

Convergence achieved
$\Rightarrow$ calculate $\mathbf{q}_\mu^{(i)}$ from
$\mathbf{q}_\mu^{(i)} = \sum_{j=1}^{i} C_{\mu,j}^{(i)}\mathbf{b}_j^{(i)}$ ④

M. Reiher, J. Neugebauer, J. Chem. Phys. *118* **2003** 1634

Mode-Tracking: Calculation of Davidson Matrix

- How to calculate $\tilde{\mathbf{H}}^{(i)} = \mathbf{B}^{(i)T}\mathbf{H}\mathbf{B}^{(i)}$ without knowing $\mathbf{H}$?

- Trick: Define matrix $\mathbf{\Sigma}^{(i)} = \mathbf{H}\mathbf{B}^{(i)}$

- Calculate elements by applying chain rule for differentiation:

$$\Sigma_{jI}^{(i)} = \sum_{J} \left(\frac{\partial^2 E_{el}}{\partial R_I \partial R_J} \right)_0 B_{jJ}^{(i)} = \left(\frac{\partial^2 E_{el}}{\partial R_I \partial \mathbf{b}_j} \right)_0 = \left[\frac{\partial}{\partial \mathbf{b}_j} \left(\frac{\partial E_{el}}{\partial R_I} \right) \right]_0$$

$\Rightarrow$ $\Sigma_{jI}^{(i)}$ can be calculated as numerical derivative of gradient component I along the basis vector $\mathbf{b}^j$ (analytic scheme also possible)

- ... this is done *semi-numerically* by the program $\textsc{Akira}$:
  http://www.reiher.ethz.ch/software/akira

Mode-Tracking Program Structure
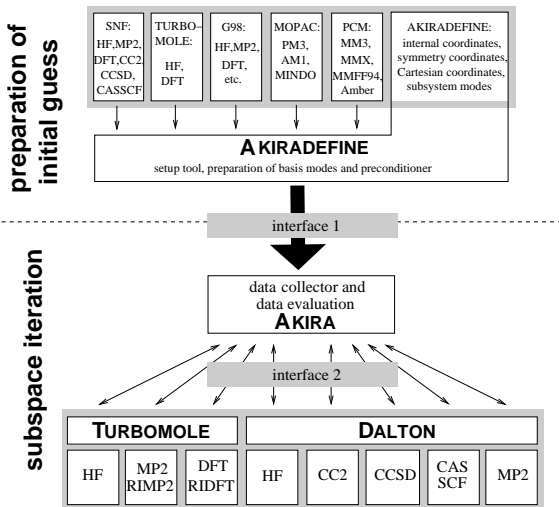
Interfaces to other codes (Gaussian, ADF) also implemented.

Mode-Tracking Convergence and Stability

These issues have been investigated in detail:

- numerical accuracy
- preconditioning
- different choices for the guessed vibration
- convergence to the complete spectrum
- implicit restriction to symmetry species
- near-degenerate vibrations
- intermolecular vibrations
- noncharacteristic vibrations

M. Reiher, J. Neugebauer, Phys. Chem. Chem. Phys. *6* **2004** 4621
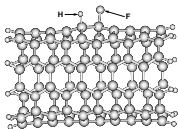
Mode-Tracking for Carbon Nanotubes
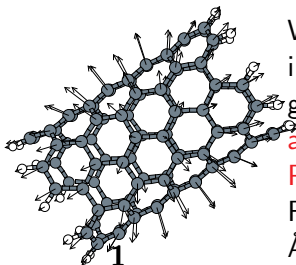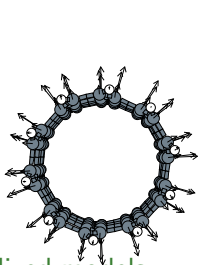
Wavenumbers of breathing modes in cm^{-1}:
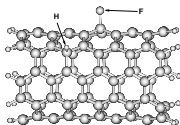
guesses: inverse Hessian and normal modes from PM3
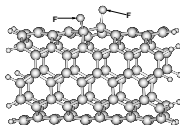
Raman activity S in Å^4/amu.

functionalized models:



2a
HF in 1,2-position

2b
HF in 1,4-position

3
F$_2$ in 1,2-position

tube	$\tilde{\nu}_{\mathsf{sel}}$	i	S
1	341.5	1	149.4
2a	345.4	7	26.6
2b	342.7	7	89.2
3	335.0	12	84.8

M. Reiher, J. Neugebauer, J. Chem. Phys. *118* **2003** 1634

Coupling of Core Vibrations with Bulky Ligands

- breathing vibration of $[Au_6C]$ kernel in Schmidbaur's cluster in cm^{-1}
- start: octahedral distortion of $[Au_6]$
- optimization of this start for the analysis of ligand–kernel couplings
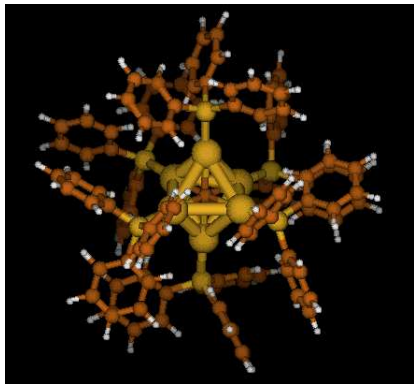
| it.#	contrib.	$|C_{i,\text{conv.}}|$	$\tilde{\nu}^{(i)}_{\text{appr.}}$
1	Au	0.992	168.7
2	P	0.124	159.6
3	C	0.005	159.0

- convergence after 3 iterations
  6 single-point calcs
- standard: 1266 single points
  (211 atoms)

J. Neugebauer, M. Reiher, J. Comput. Chem. *25* **2003** 587

Mode-Tracking Sub-System Methodology

Molecular wires and 'one-dimensional' bridges:

- normal modes and frequencies for motions of the carbon chain in Gladysz' $\{Re\}_2$-polyynediyl complexes
- frequency of the mode shown below: 55 cm^{-1} after 2 iterations ($\hat{=}$ 4 single-point calculations instead of 864 for the full system)
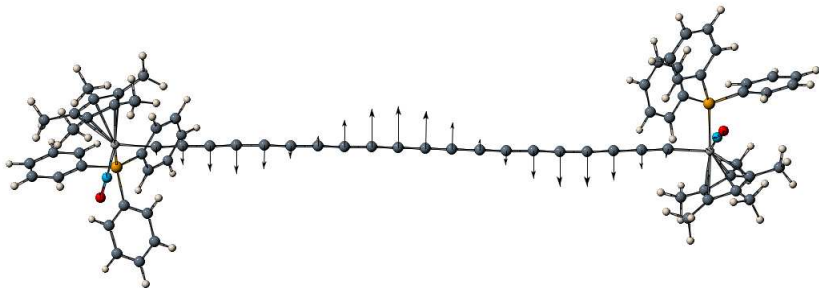
J. Neugebauer, M. Reiher, J. Phys. Chem. A *108* **2004** 2053

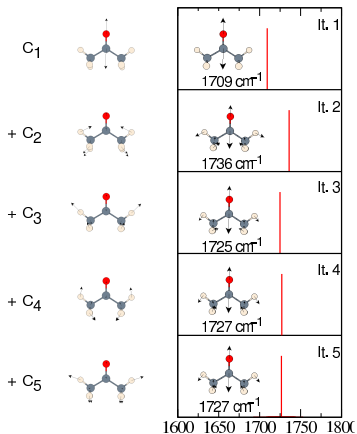# Mode-Tracking: More Applications
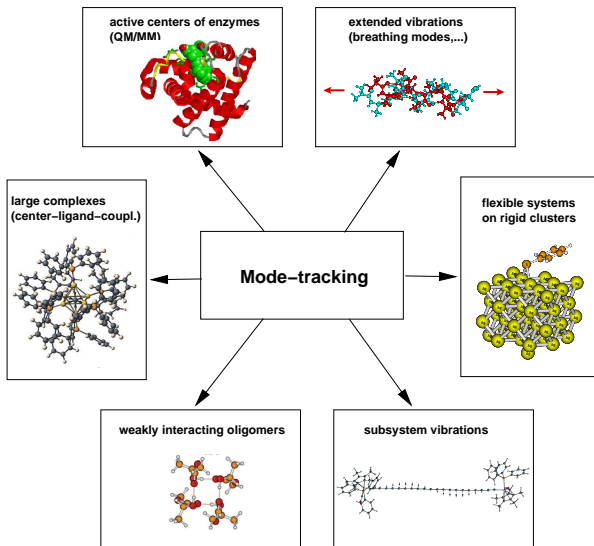
For Refs. see: C. Herrmann, J. Neugebauer, M. Reiher, New J. Chem. *31* **2007** 818

IR Spectra: methods for large molecules

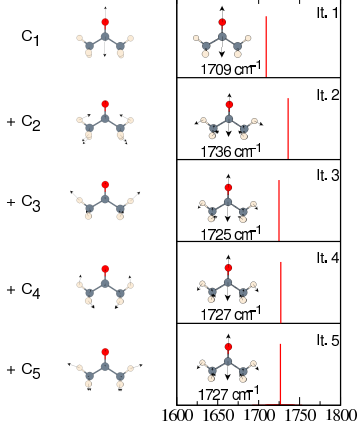Mode tracking

construct
intuitive guess

c_1

It. 1
1709 cm^{-1}

+ c_2

It. 2
1736 cm^{-1}

+ c_3

It. 3
1725 cm^{-1}

+ c_4

It. 4
1727 cm^{-1}

+ c_5

It. 5
1727 cm^{-1}

1600 1650 1700 1750 1800

iterative refinement
of particular normal modes

New vibrational methods: **Intensity-Tracking**

Mode tracking

construct
intuitive guess

Intensity tracking

construct artificial
mode of maximum
intensity

iterative refinement
of particular normal modes
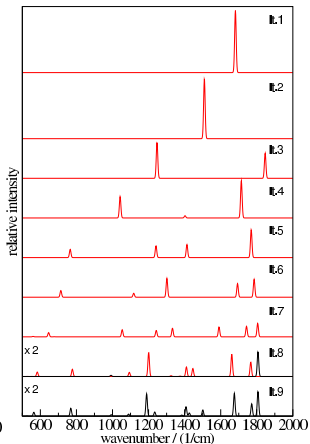
iterative refinement
of the spectrum

How Find a Starting Distortion?: Intensity-Carrying Modes

1. hypothetical modes $\boldsymbol{L}_k$ with maximum intensity

2. first considered for infrared spectroscopy
   📄 H. Torii, *et al.*, J. Phys. Chem. A *103* **1999** 5557;
   S. Luber, J. Neugebauer, M. Reiher, J. Chem. Phys. *130* **2009** 064105

3. most efficiently exploited for Resonance Raman
   📄 K. Kiewisch, J. Neugebauer, M. Reiher, J. Chem. Phys. *129* **2008** 204103

4. Raman- and Raman Optical Activity (ROA) Intensity-Carrying Modes (ICMs) determined by an eigenvalue problem:
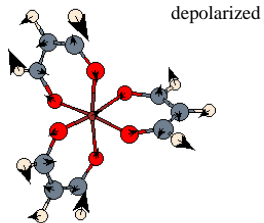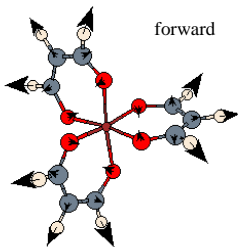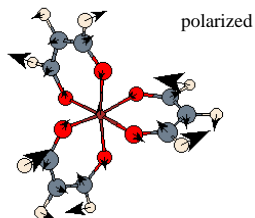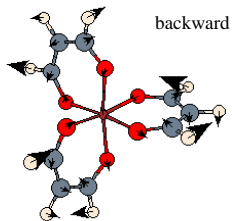
   $$\boldsymbol{M}\boldsymbol{L}_k = a_k \boldsymbol{L}_k$$

   eigenvalue a_k proportional to ROA intensity;

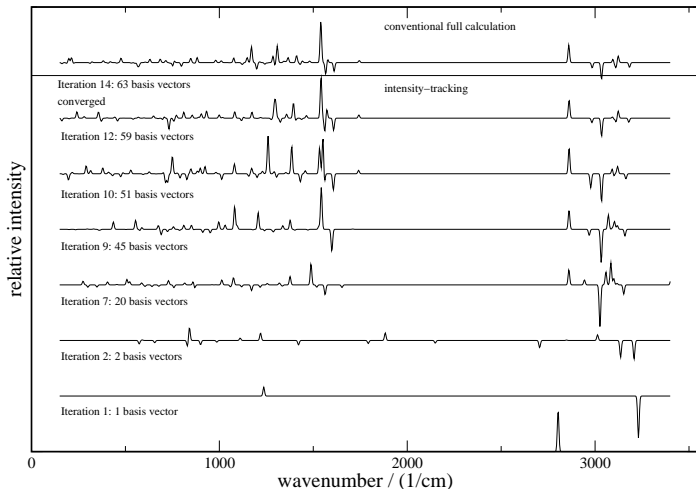 $\boldsymbol{M}$ contains Cartesian derivatives of ROA tensor components
   📄 S. Luber, M. Reiher, ChemPhysChem *10* **2009** 2049

ROA-ICMs of Λ-Tris(propane-1,3-dionato)cobalt(III)

ROA Intensity-Tracking for L-Tryptophan

selective calculation of normal modes with high ROA intensity

S. Luber, M. Reiher, ChemPhysChem *10* **2009** 2049

Introducing New Analysis Tool: Localized Modes

1. consider a subset of normal modes Q^{sub}

2. transform to new set of modes by unitary transformation U

$$\tilde{Q}^{\mathsf{sub}}_{i\alpha,p} = \sum_q U_{qp} Q^{\mathsf{sub}}_{i\alpha,q}$$

3. define a criterion $\xi(\tilde{Q}^{\mathsf{sub}})$ that measures "how localized the transformed modes are", e.g.,

$$\xi_{\mathsf{at}}(\tilde{Q}^{\mathsf{sub}}) = \sum_p \sum_i (\tilde{C}^{\mathsf{sub}}_{ip})^2 \quad \text{with} \quad \tilde{C}^{\mathsf{sub}}_{ip} = \sum_{\alpha=x,y,z} (\tilde{Q}^{\mathsf{sub}}_{i\alpha,p})^2$$
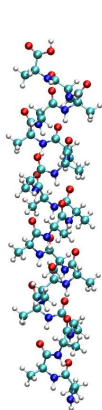
4. determine U such that $\xi(\tilde{Q}^{\mathsf{sub}})$ is maximized (using consecutive Jacobi rotations)
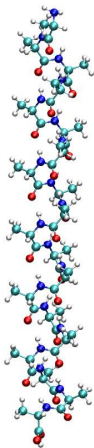
Ch.R. Jacob, M. Reiher, J. Chem. Phys. *130* **2009** 084106

Example: Models of α-Helix and 3_{10}-Helix

Model system: (all-S)–(Ala)$_{20}$



α-helix 3_{10}-helix

- polypeptide containing 20 alanine (simplest chiral amino acid)

- 203 atoms

- two conformations:
  - α-helix
  - 3_{10}-helix

- geometry fully optimized

- solvent effects not considered

Ch. R. Jacob, S. Luber, M. Reiher, Chem. Eur. J. **15** (2009) 13491.

Localized Vibrations: Amide I Band

- Normal modes:
  - Delocalized combination of vibrations on several residues

- Localized modes:
  - Localized modes on different residues are very similar

  - Deviations only at the termini

  ⇒ **it is sufficient to consider only one representative localized mode**

  - Vibration of a single residue

  ⇒ **it is sufficient to show the atoms of only one residue**
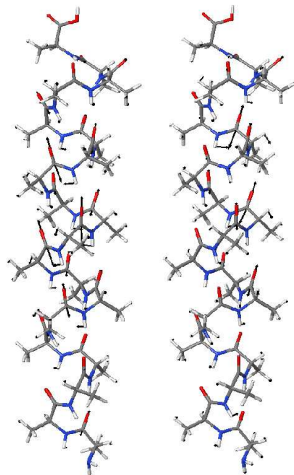
1660.4 cm^{-1} 1663.4 cm^{-1}

Ch. R. Jacob, M. Reiher, J. Chem. Phys. **130** (2009) 084106.

α-Helix: Comparison with Experimental Spectra

Amide I band
- excellent agreement of band position and intensities (amide I couplet)

CH$_3$ bending bands
- excellent agreement of band position and intensities

Extended amide III region
- good agreement of band positions
- some differences for shapes and intensities
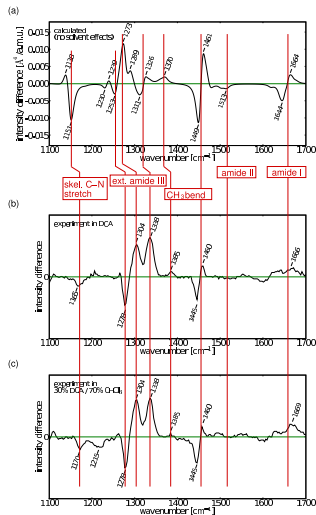- $\Rightarrow$ analyzed recently in more detail

  📄 Th. Weymuth, Ch. R. Jacob, M. Reiher, J. Phys. Chem. B **114** (2010) 10649
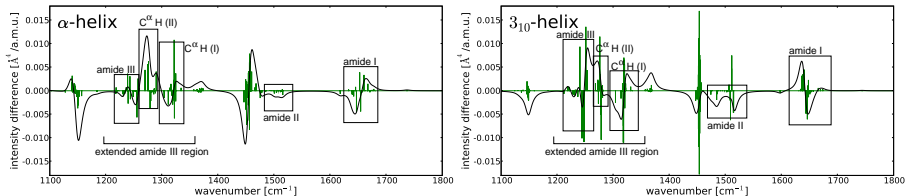
experimental spectra from:

📄 I.H. McColl *et al.*, J. Am. Chem. Soc. **126** (2004), 8181.

Analysis of Calculated ROA Spectra

How are changes in the ROA spectra related to helix structure?

- which vibrations and which atoms contribute to each band?
- how do the total band intensities arise?
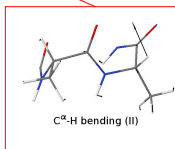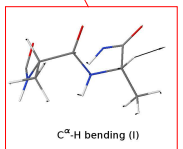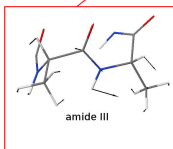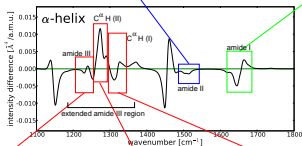- what determines the individual band shapes?

Problems with such an analysis

- several normal modes contribute to each band
- each of these normal modes is delocalized over the whole helix

⇒ **transformation to "localized modes"**

Visualization of Localized Modes

Consideration of only one representative localized mode necessary
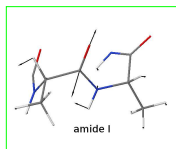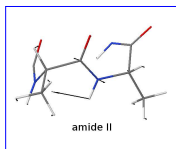
- Amide I:

  C=O stretching

- Amide II:

  N–H bending and
  C–N stretching

- Ext. Amide III:

  mixing between
  N–H bending and
  C^{α}–H bending

**Note: Localized
modes differ from
normal modes of small
model building blocks!**

Analysis of Band Shapes

Why is the amide I couplet opposite in the α-helix and the 3_{10}-helix?

- localized modes almost identical for α-helix and 3_{10}-helix
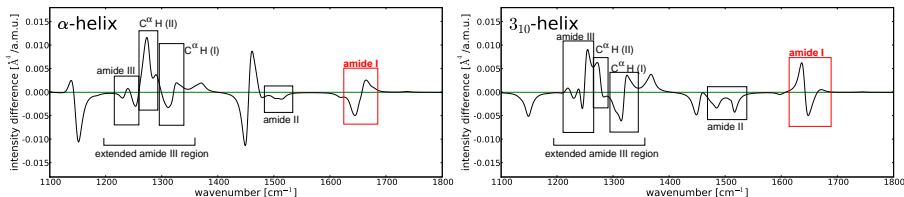- intensities of localized modes and total intensities very similar

Decompose ROA intensities of normal modes

$$I_p = \sum_{qr} U_{pq} U_{pr} [\tilde{I}]_{qr}$$

- U_{pq}: coefficient of qth localized mode in pth normal mode
- $[\tilde{I}]_{qr}$: intensity coupling matrix

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Analysis of Band Shapes

Amide I (vibrational) coupling matrices

- α-**helix:**

  α-helix

  nearest-neighbor
  coupling largest

  3rd nearest-neighbor
  coupling significant

  $$\begin{pmatrix} 1659.1 & 8.5 & -2.2 & -4.2 & -0.4 & -0.5 \\ 8.5 & 1655.9 & 7.9 & -2.3 & -4.2 & -0.4 \\ -2.2 & 7.9 & 1654.6 & 8.2 & -2.2 & -4.4 \\ -4.2 & -2.3 & 8.2 & 1654.9 & 8.3 & -2.1 \\ -0.4 & -4.2 & -2.2 & 8.3 & 1654.8 & 8.2 \\ -0.5 & -0.4 & -4.4 & -2.1 & 8.2 & 1655.8 \end{pmatrix}$$

- 3_{10}-**helix:**

  3_{10}-helix

  2nd nearest-neighbor
  coupling largest

  3rd nearest-neighbor
  coupling small

  $$\begin{pmatrix} 1643.1 & 2.5 & -3.7 & -0.7 & -0.6 & -0.6 \\ 2.5 & 1641.8 & 2.7 & -3.7 & -0.8 & -0.6 \\ -3.7 & 2.7 & 1640.4 & 2.8 & -3.8 & -0.8 \\ -0.7 & -3.7 & 2.8 & 1641.7 & 2.4 & -3.7 \\ -0.6 & -0.8 & -3.8 & 2.4 & 1640.5 & 2.5 \\ -0.6 & -0.6 & -0.8 & -3.7 & 2.5 & 1641.1 \end{pmatrix}$$

$\rightarrow$ **different coupling matrices directly related to helix structures**

Analysis of Band Shapes
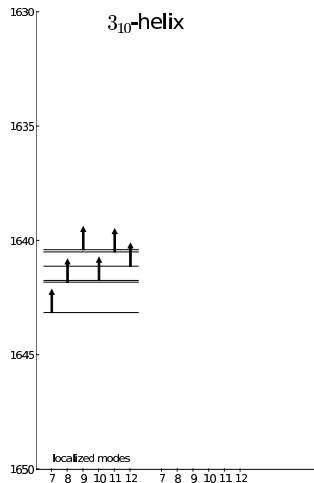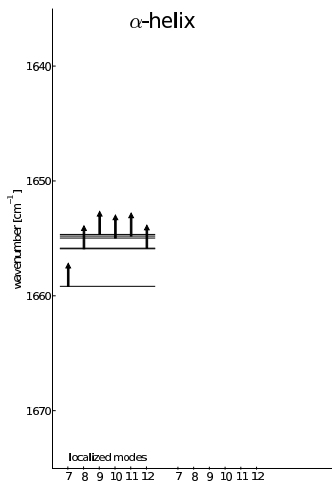
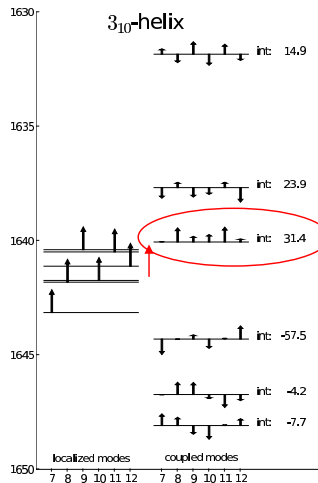## Coupling of localized amide I modes
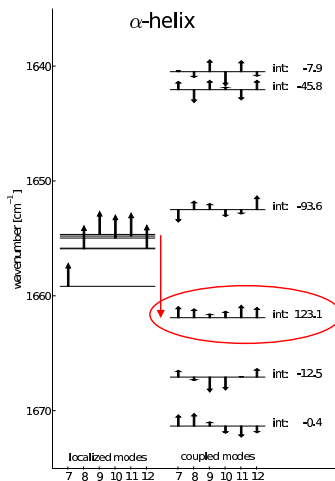
Analysis of Band Shapes

Coupling of localized amide I modes

α-**helix**:

in-phase combination
shifted to **higher**
wavenumbers

3_{10}-**helix**:

in-phase combination
shifted to **lower**
wavenumbers

$\Rightarrow$ **different structure of coupling matrix $\tilde{\Omega}$ explains opposite couplets**

Concluding remarks

"[...] work along these lines will eventually replace the still needed chemical intuition — i.e. the profound knowledge of the experimentally working chemists — in the design of chemical reactions and reactants.
[by]
Purpose-driven algorithms like Mode-Tracking [and Intensity-Tracking] represent a new generation of quantum chemical methods. More of them will surely become available because of the tremendously increased computational power of desktop computers that allows us to loosen the corset of the efficiency paradigm which governs the derivation and implementation of quantum-chemical equations solely focused on their fast solution for ever-increasing molecular sizes."

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**Relativistic
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